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Representation of CO_2 absorption in sterically hindered amines

Zulkifli Idris[a]* and Dag A. Eimer[a,b]

[a]*Telemark University College, Kjølnes Ring 56, Porsgrunn 3918, Norway*
[b]*Tel-Tek, Kjølnes Ring 30, Porsgrunn 3918, Norway*

Abstract

Post-combustion capture technology implemented at carbon-rich power plants offers an alternative for mitigating CO_2 emissions. Aqueous alkanolamines such as monoethanolamine and *N*-methyldiethanolamine are utilized to chemically absorb CO_2. However, current laboratory practice for evaluating new absorbents is laborious and time consuming. In this paper, we presented a possible relationship between acid dissociation constant, K_a and the CO_2 absorption affinity of sterically hindered amines. We demonstrated that addition of hydroxyl and methyl groups to AMP decreases the absorption affinity of sterically hindered amines towards CO_2. This finding adds to our understanding in trying to find a new and better CO_2 absorbent.

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Keywords: Carbon dioxide; sterically hindered amines; absorption equilibrium

1. Introduction

Combustion of fossil fuels releases carbon dioxide (CO_2) into the atmosphere. The high amount of CO_2 produced from human activities is considered to be one of the main contributors of greenhouse gas emission which could lead to the global warming phenomena [1]. CO_2 absorb some of the heat released by the Earth, and concurrently, the CO_2 molecules enter into excited mode and become unstable. The molecules released the extra energy back into the atmosphere, which could contribute to the rise in the Earth temperature i.e. global warming.

* Corresponding author. Tel.: +47 3557 5188; fax: +47 3557 5001.
E-mail address: Zulkifli.B.Idris@hit.no

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In Nature, the production and consumption of CO_2 is balanced by microorganisms, plants and animals through the carbon cycle, as illustrated in Figure 1 [1]. Human activities altered the CO_2 balance by adding more CO_2 into the atmosphere, whilst influencing the removal of CO_2 from the atmosphere as exemplified by deforestation.

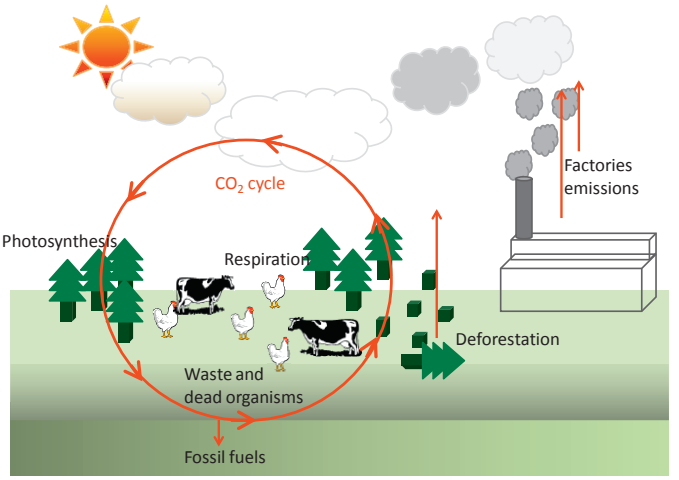

Fig. 1. The Carbon cycle.

The United Nations, through several of its treaties for example the Kyoto Protocol and Copenhagen Accord has recommended that countries are to contribute in minimizing the emission of greenhouse gases. One alternative to mitigate CO_2 emissions is to apply Carbon Capture and Storage (CCS) technology. In CCS, CO_2 is captured from power plants and then stored underground for long periods of time. There are three approaches to capture CO_2 generated from power plants activities i.e. pre-combustion, post-combustion and oxy-fuel combustion. The CO_2 present in synthesis gas is separated before the gas enters a combustion turbine in pre-combustion capture technology [2]. In post-combustion capture, CO_2 is separated from flue gas after complete burning of the fuel [3]. Finally, in oxy-combustion capture, the fuel is burned with O_2 separated from the air which results in a more 'clean' final flue gas, which contains H_2O and concentrated CO_2, where the condensation of H_2O renders pure CO_2 [4].

Post-combustion capture technology is important as it is compatible with the existing power plants without requiring substantial modifications to the plants. Several approaches for capturing CO_2 have been studied such as physical and chemical absorption, adsorption and membrane techniques. However, it is generally accepted that the chemical absorption technique is the most applicable for CO_2 capture, at least in the shorter term [5]. In this technique, a solution (solvent) is used to absorb CO_2 from the exhaust after combustion. The absorbed CO_2 is then liberated from the solvent before transportation and storage.

The most established class of solvent for CO_2 absorption is aqueous alkanolamines [5]. These amines contain at least one hydroxyl group, and are characterised based on the number of free hydrogen atom attached to the Nitrogen atom of the compound i.e. primary, secondary and tertiary. A list of commonly used alkanolamines is shown in Table 1.

Table 1. Commonly used alkanolamines for CO_2 absorption, as reported in the literature.

Name	Class	pK_a value (25 °C) [6]
Monoethanolamine (MEA)	1	9.45
Diethanolamine (DEA)	2	8.88
N-methyldiethanolamine (MDEA)	3	8.52
Diisopropanolamine (DIPA)	2	9.00
Diglycolamine (DGA)	1	9.46

Primary and secondary amines form a zwitterion upon encountering a CO_2 molecule (equation 1) [7, 8].

$$RR'NH + CO_2 \leftrightarrow RR'NH^+COO^- \text{ (Zwitterion)} \quad (1)$$

The reaction then proceeds with the formation of carbamate complex (equation 2). A bicarbonate ion and a free amine molecule for further reaction with the CO_2 are formed when a carbamate complex reacts with a water molecule (equation 3).

$$RR'NH^+COO^- + RR'NH \leftrightarrow RR'NCOO^- \text{ (carbamate)} + RR'NH_2^+ \quad (2)$$

$$RR'NCOO^- + H_2O \leftrightarrow RR'NH + HCO_3^- \quad (3)$$

Tertiary amines, on the other hand, due to the lack of free hydrogen atom, are unable to react directly with the CO_2 molecules. Instead, the reaction proceeds with the formation of bicarbonate through base-catalysis mechanism (equation 4) [9].

$$R_3N + H_2O + CO_2 \leftrightarrow R_3N^+H + HCO_3^- \quad (4)$$

Sterically hindered amines have also been proposed as possible absorbents for CO_2 capture. Sartori and Savage defined sterically hindered amines as any primary or secondary amines with the amino group attached to a tertiary carbon, and such an example is 2-amino-2-methyl-1-propanol (AMP) [10]. Several research groups have studied kinetics and CO_2 solubility in different sterically hindered amines and discovered that these amines are generally better at absorbing CO_2 than MEA [10-13]. The presence of a bulky tertiary carbon adjacent to the amino functional group meant that these amines only formed unstable carbamates, providing a faster reaction with CO_2 than tertiary amines while lowering the cost for solvent regeneration.

It is desirable to identify more efficient absorbents, while utilizing available absorbents effectively. However, one obstacle to finding new absorbents is the challenge to establish reliable CO_2 equilibrium data which is necessary for initial process evaluations as well as for process optimization and for making accurate estimates of process equipment and energy needed. The current approach for obtaining CO_2 equilibrium data is to collect a lot of data in the laboratory. The data are then validated by comparing with the well-established equilibrium data. These procedures are laborious and time consuming, and hence are limiting our ability to find better absorbents. In our laboratory, we are developing techniques to establish CO_2 absorption equilibrium data with the aim to outline characteristics of good absorbents and through these identifying new absorbents. This paper aims to find a possible contributing factor that makes sterically hindered amines a better candidate than normal aliphatic alkanolamines for CO_2 capture.

2. Possible relationship between pK_a of selected sterically hindered amines and their affinity for CO_2 absorption.

We have performed an extensive literature search of the available CO_2 solubility data for sterically hindered amine (examples are shown in Table 2). The most studied sterically hindered amine is AMP. AMP is a three-carbon chain alkanolamine, with an amino and methyl attached to the carbon atom at beta position. Addition of other functional groups such as methyl and hydroxyl produced new sterically hindered amines, as demonstrated in Figure 2 e.g. AHPD, AMPD and AEPD.

The solubility of CO_2 in aqueous AMP was measured by several research groups since established as a potential candidate by Sartori and Savage [10, 12, 14, 15]. Baek and Yoon studied the solubility of CO_2 at equilibrium with aqueous AMPD at different temperatures and concentrations in 1998 [16]. They found that the solubility of CO_2 in AMPD is similar to MDEA. Lee and coworkers measured the solubility of CO_2 in AEPD and AHPD in 2002, and

claimed that these amines have a higher loading capacity of CO_2 than MEA and AMPD at higher partial pressures [17, 18].

Table 2. pK_a values of sterically hindered amines investigated in this paper.

Name	pK_a (25 °C) [6]
2-amino-2-methyl-1-propanol (AMP)	9.82
2-amino-2-hydroxymethyl-1,3-propanediol (AHPD)	8.03
2-amino-2-methyl-1,3-propanediol (AMPD)	8.76
2-amino-2-ethyl-1,3-propnaediol (AEPD)	8.80

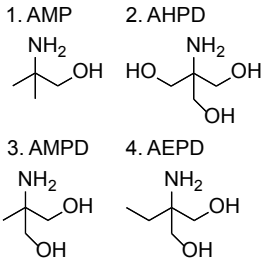

Fig. 2. Sterically hindered amines investigated in this paper.

Whilst the addition of hydroxyl group makes the alkanolamine more soluble in water, it also changed the properties of the amines. One of the chemical properties of the amine that will change upon addition of functional group is the acid dissociation constant, K_a or normally quoted in logarithmic value as pK_a. The K_a is a measure of the strength of an acid in solution; a stronger acid have a higher K_a value (low pK_a value) compared to a weaker acid. Due to the fact that the reaction between a molecule of amine and CO_2 is an acid-base reaction, pK_a plays an important role. Thus the ability to predict the relationship between pK_a and CO_2 absorption of amines might give us insight into understanding the characteristics of good CO_2 absorbents.

To examine the effect of pK_a on the CO_2 affinity of AMP, AMPD, AEPD and AHPD, we have compared the equilibrium CO_2 partial pressures of these amines at the same temperature and loading, which represents the affinity of CO_2 for these amines. A possible relationship between pK_a and CO_2 absorption affinity of sterically hindered amines closely related to AMP is illustrated in Figure 3. At 0.7 mol/mol loading and 10 wt%, AMP has the lowest reported CO_2 partial pressure. The low CO_2 partial pressure (corresponding to the amount of CO_2 present in the gas phase, as compared to the liquid phase) indicates that AMP, which has the highest pK_a value among these sterically hindered amines, absorbs more CO_2 in the liquid phase. Meanwhile AHPD, which has the lowest pK_a among these sterically hindered amines, has the highest partial pressure of CO_2 in the gas phase. This finding suggests that amines with high pK_a value may be a good candidate for a better CO_2 absorbent. It also shows that addition of methyl and hydroxyl groups to AMP decreases the absorption affinity of these sterically hindered amines towards CO_2. In a patent filed by Cansolv, they explained that amines with pK_a values of more than 7.5 are suitable candidates for CO_2 absorption [19]. The importance of pK_a in deciding the best amine for CO_2 capture has also been explored by Khalili et al in which they substituted piperazine molecule with alkyl and hydroxyl functional groups [20]. They discovered that these functional groups introduced a hindrance effect to piperazine, resulting in much lower pK_a values.

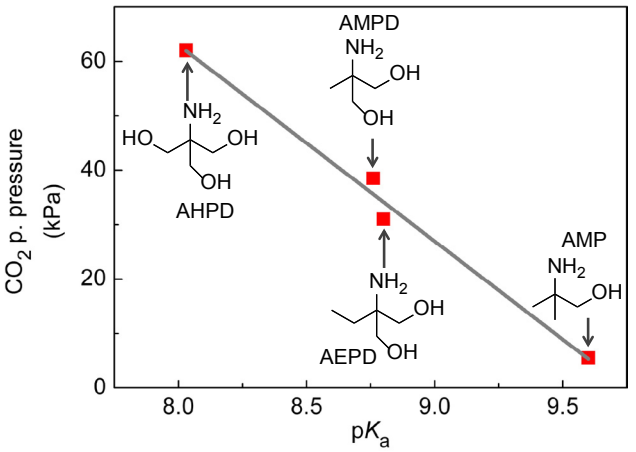

Fig. 3. A possible relationship between pK_a and CO_2 absorption affinity for sterically hindered amines. All data points are of the same temperature (40 ^oC), CO_2 loading (0.7 mol CO_2/mol amine) and concentration (10 wt%) [16-18].

Further comparison with amines from the same class (primary) was also performed and the result is shown in Figure 4. As can be seen, there is a possible relationship between the pK_a values of amines and the amount of CO_2 absorbed in the gas phase for amines of the same class. One exception is clear; although MEA has a slightly lower pK_a value than AMP (which technically if considering pK_a as the only factor for CO_2 absorption, one would speculate that MEA will have a higher CO_2 partial pressure at a constant loading in comparison to AMP), Figure 4 shows that the CO_2 partial pressure of MEA is also slightly lower than that of AMP. We attributed this deviation to other factors that would contribute to the CO_2 absorption [21, 22]. This indicates that although pK_a does to some extent affect the CO_2 absorption of amines, one must be careful in reporting the data to avoid over-interpretation.

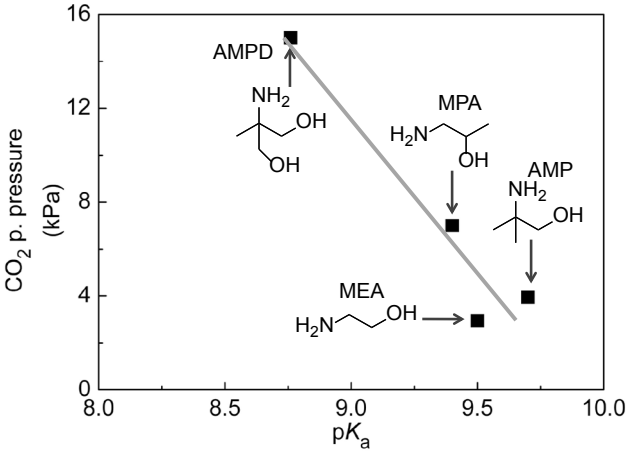

Fig. 4. Comparison of pK_a values and CO_2 absorption affinity for other amines. All data points are of the same temperature (40 ^oC), concentration (30 wt%) and mol/mol loading (0.5) [16, 23-25].

3. Conclusion

In this paper, we have demonstrated that there is a relationship between the pK_a and CO_2 absorption affinity. Additions of functional groups have also lowered the pK_a values of AMPD, AHPD and AEPD. In general, when choosing an amine for CO_2 absorption, the pK_a value of the amine should be taken into consideration.

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